NATURE OF ACIDS & BASES

General Properties:

	ACIDS	BASES
Taste	sour	Bitter
Change color of indicators	→	↓
Blue Litmus	turns red	no change
Red Litmus	no change	turns blue
Phenolphtalein	Colorless	turns pink
Neutralization	React with bases to form salt and water	React with acids to form salt and water

• Listed below are some common acids and their common uses:

TABLE 15.1 Some Common Acids		
Name	Occurrence/Uses	
Hydrochloric acid (HCI)	Metal cleaning; food preparation; ore refining; primary component of stomach acid	
Sulfuric acid (H_2SO_4)	Fertilizer and explosives manufacturing; dye and glue production; automobile batteries; electroplating of copper	
Nitric acid (HNO ₃)	Fertilizer and explosives manufacturing; dye and glue production	
Acetic acid $(HC_2H_3O_2)$	Plastic and rubber manufacturing; food preservative; active component of vinegar	
Citric acid $(H_3C_6H_5O_7)$	Present in citrus fruits such as lemons and limes; used to adjust pH in foods and beverages	
Carbonic acid (H ₂ CO ₃)	Found in carbonated beverages due to the reaction of carbon dioxide with water	
Hydrofluoric acid (HF)	Metal cleaning; glass frosting and etching	
Phosphoric acid (H ₃ PO ₄)	Fertilizer manufacture; biological buffering; preservative in beverages	

NATURE OF ACIDS & BASES

• The structural formulas for several common acids are shown below. Note that all acids have a hydrogen bonded to an oxygen (referred to as the acidic hydrogen) that ionizes in aqueous solutions.



• Acetic acid is an organic acid that contains the *carboxylic acid* group, that is shown below:



• Some common bases are listed below. Organic bases (called alkaloids) are also bitter in taste and are often poisonous.



TABLE 15.2 Common Bases	
Name	Occurrence/Uses
Sodium hydroxide (NaOH)	Petroleum processing; soap and plastic manufacturing
Potassium hydroxide (KOH)	Cotton processing; electroplating; soap production; batteries
Sodium bicarbonate (NaHCO ₃)	Antacid; ingredient of baking soda; source of $\rm CO_2$
Sodium carbonate (Na ₂ CO ₃)	Manufacture of glass and soap; general cleanser; water softener
Ammonia (NH ₃)	Detergent; fertilizer and explosives manufacturing; synthetic fiber production

DEFINITION OF ACIDS & BASES

• There are three definitions of acids and bases used in chemistry. Each definition is useful in a given instance, and are discussed next.

Arrhenius Definition:

- *Arrhenius* definition of acids and bases in based on their behavior in water (aqueous solutions), and was developed by Swedish chemist Svante Arrhenius.
- Based on this definition:
 - \blacktriangleright *Acid*: A substance that produces H⁺ ions in aqueous solution.
 - **Base**: A substance that produces OH⁻ ions in aqueous solution.
- Therefore, according to the Arrhenius definition, HCl is an acid because it produces H⁺ ions in solution:

 $HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$

- The H⁺ ions produced are very reactive and bond to water molecules in aqueous solution, forming H₃O⁺:
 - $\mathbf{H}^{+} + : \overset{\mathbf{H}}{\odot} : \mathbf{H} \longrightarrow \begin{bmatrix} \overset{\mathbf{H}}{\mathbf{H}} \\ \mathbf{H} : \overset{\mathbf{H}}{\odot} : \mathbf{H} \end{bmatrix}^{+}$
- Similarly, according to the Arrhenius definition, NaOH is a base because it produces OH⁻ in solution.

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

• Based on Arrhenius definition, acids and bases combine to form water, neutralizing each other in the process:

$$H^{+}(aq) + OH^{-}(aq) \longrightarrow H_2O(l)$$







DEFINITION OF ACIDS AND BASES

Brønsted-Lowry Definition:

- The *Brønsted-Lowry* definition of acids and bases focuses on the transfer of H⁺ ions in an acid-base reaction. Since H⁺ is a proton, this definition focuses on the idea of proton donor and proton acceptor:
 - \blacktriangleright *Acid*: proton (H⁺ ion) donor
 - > **Base**: proton (H^+ ion) acceptor
- According to this definition, HCl is an acid because, in solution, it donates a proton to water:

 $HCl (aq) + H_2O (l) \longrightarrow H_3O^+ (aq) + Cl^- (aq)$

• According to this definition, NH₃ is a base because, in solution, it accepts a proton from water:

 $NH_3(aq) + H_2O(l) \longrightarrow NH_4^+(aq) + OH^-(aq)$

• According to the Brønsted-Lowry definition, acids (proton donors) and bases (proton acceptors) always occur together in an acid-base reaction. For example:

 $\begin{array}{rcl} HCl (aq) & + & H_2O (l) & \longrightarrow & H_3O^+ (aq) & + Cl^- (aq) \\ acid & & base \\ (proton \ donor) & (proton \ acceptor) \end{array}$

$NH_3(aq) +$	$H_2O(l) \iff$	$+ NH_4^+(aq) + OH^-(aq)$
base	acid	
(proton acceptor)	(proton donor)	

• According to the Brønsted-Lowry definition, some substances-such as water-can act as acids or bases. These substances are called *amphoteric*.

Examples:

Identify the Brønsted-Lowry acid and base in each of the following equations:

- $1. \qquad C_6H_5OH \ + C_2H_5O^- \ \longrightarrow \ C_6H_5O^- \ + \ C_2H_5OH$
- $2. \qquad H_2O \ + \ Cl^- \ \longrightarrow \ HCl \ \ + \ \ OH^-$

DEFINITION OF ACIDS AND BASES

• In a reversible acid-base reaction, both forward and reverse reactions involve H⁺ transfer



• The pair of acid and base from each side of these reactions are referred to as *acid-base conjugate pairs*. A *conjugate acid* is any base to which a proton has been added, while a *conjugate base* is any acid from which a proton has been removed.



Examples:

1. Identify the Brønsted-Lowry acid-base conjugate pairs in each of the following equations:

a)
$$H_2SO_4(aq) + H_2O(l) \longrightarrow HSO_4^-(aq) + H_3O^+(aq)$$

- b) $HCO_3^-(aq) + H_2O(l) \longrightarrow H_2CO_3(aq) + OH^-(aq)$
- 2. Which pair is not a conjugate acid-base pair?
 - a) $(CH_3)_3N; (CH_3)_3NH^+$ b) $H_2SO_4; H_2SO_3$ c) $HNO_2; NO_2^-$

LEWIS ACIDS AND BASES

- A third definition of acids and bases is the Lewis model, which further broadens the range of substances that can be considered acids and bases.
- This model, developed by Gilbert Lewis, defined acids and bases in terms of electron-pair transfer.

 $H^{+} + : NH_{3} \longrightarrow \left[H: NH_{3}\right]^{+}$ Brønsted–Lowry model Lewis model focuses focuses on the proton on the electron pair

- Therefore, based on the Lewis model:
 - > *Lewis Acid*: electron pair acceptor
 - Lewis Base: electron pair donor



- The Lewis model does not substantially expand the substances that can be considered a base, since a proton acceptor must have an electron pair to bond the proton.
- However, it does significantly expand the substances that can be considered an acid. According to this model, substances need not even contain hydrogen to be an acid. For example:

LEWIS ACIDS AND BASES

• Since molecules with incomplete octets have empty orbitals, they can serve as Lewis acids. For example, both AlCl₃ and BF₃ have incomplete octets:



• As a result, both these molecules can act as Lewis acids, as shown below:





• Some molecules that do not initially contain empty orbitals can rearrange their electrons to act as Lewis acids. For example, consider the reaction between water and carbon dioxide:



LEWIS ACIDS AND BASES

• Some cations, since they are positively charged and have lost electrons, have empty orbitals that allow them to also act as Lewis acids. For example, consider the hydration of Al³⁺ ions shown below:

$$Al^{3+}(aq) + 6\begin{bmatrix} H\\ |\\ :O:\\ |\\ H\end{bmatrix}(l) \longrightarrow Al\begin{bmatrix} H\\ |\\ :O:\\ |\\ H\end{bmatrix}_{6}^{3+}(aq)$$
Lewis base

• In General:

LEWIS ACIDS	LEWIS BASES
electron pair acceptors	electron pair donors
Usually positive ions or electron	Usually negative ions or molecules
deficient molecules	with lone pairs
NEUTRALIZATION: A reaction in which an electron pair is transferred	

Examples:

- 1. Classify each species below as a Lewis acid or a Lewis base:
 - a) BeCl₂
 - b) OH⁻
 - c) $B(OH)_3$
 - d) CN^{-}

ACIDS & BASES: LEWIS VS. BRONSTED-LOWRY

- The Bronsted-Lowry and Lewis definitions of acids and bases are complementary and are often used to explore the common ways in which acids and bases are involved in many reactions.
- The general reaction schemes below show the difference between the two definitions.



- Note that in the Bronsted-Lowry definition, the acid exchanges proton with the base, and as a result forms charged species as product. In the Lewis definition, however, the product formed is an adduct of the acid and base, and is charge neutral.
- The specific examples below show this difference



Н

Lewis

ACID STRENGTH

- The strength of an electrolyte depends on the extent of its dissociation into its component ions in solution. A strong electrolyte completely dissociates into ions in solution, whereas a weak electrolyte partially dissociates into ions.
- The strength of an acid is similarly defined. A strong acid completely ionizes in solution, while a weak acid only partially ionizes. Therefore, the strength of the acid depends on the equilibrium shown below:

$$HA(aq) + H_2O(l) \implies H_3O^+(aq) + A^-(aq)$$

• For example, hydrochloric acid (HCl) is classified as a strong acid since its solution contains virtually all ions:



• Listed below are six important strong acids. Note that sulfuric acid (H₂SO₄) is diprotic, while the others are monoprotic.

TABLE 15.3 Strong Acids	
Hydrochloric acid (HCl)	Nitric acid (HNO ₃)
Hydrobromic acid (HBr)	Perchloric acid (HClO ₄)
Hydriodic acid (HI)	Sulfuric acid (H ₂ SO ₄) (<i>diprotic</i>)

ACID STRENGTH

• In contrast, HF is classified as a weak acid because it does not completely dissociate in solution:



- The degree to which an acid is strong or weak depends on the attraction between the anion of the acid (the conjugate base) and the hydrogen ion, relative to the attraction of these ions to water.
- When the attraction between H⁺ and A⁻ is weak, the acid is strong. On the other hand, if the attraction between H⁺ and A⁻ is strong, the acid is weak.
- For example, in HCl, the Cl⁻ has a relatively weak attraction for H⁺- the reverse reaction does not occur to any significant extent. In HF, on the other hand, the F⁻ has a greater attraction for H⁺- the reverse reaction occurs to a significant degree.
- In general, the stronger the acid, the weaker the conjugate base, and the weaker the acid, the stronger the conjugate base.



• Listed below are some common weak acids. Note that some are diprotic and one is triprotic.

TABLE 15.4 Some Weak Acids	
Hydrofluoric acid (HF)	Sulfurous acid (H ₂ SO ₃) (<i>diprotic</i>)
Acetic acid ($HC_2H_3O_2$)	Carbonic acid (H ₂ CO ₃) (<i>diprotic</i>)
Formic acid (HCHO ₂)	Phosphoric acid (H ₃ PO ₄) (<i>triprotic</i>)

ACID IONIZATION CONSTANT (Ka)

- The relative strength of a weak acid can be quantified with the *acid ionization constant* (K_a).
- K_a is the equilibrium constant for the ionization reaction of a weak acid. For example,

$$HA (aq) + H_2O (l) \implies H_3O^+ (aq) + A^- (aq)$$
$$HA (aq) \implies H^+ (aq) + A^- (aq)$$

$$\mathbf{K}_{\mathbf{a}} = \frac{[\mathbf{H}_{3}\mathbf{O}^{+}][\mathbf{A}^{-}]}{[\mathbf{H}\mathbf{A}]} = \frac{[\mathbf{H}^{+}][\mathbf{A}^{-}]}{[\mathbf{H}\mathbf{A}]}$$

• Listed below are the acid ionization constants for some monoprotic weak acids, listed in order of decreasing strength:

Acid	Formula	Structural Formula	Ionization Reaction	Ka
Chlorous acid	HCIO ₂	H - 0 - CI = 0	$\frac{\text{HCIO}_2(aq) + \text{H}_2\text{O}(l)}{\text{H}_3\text{O}^+(aq) + \text{CIO}_2^-(aq)}$	$1.1 imes 10^{-2}$
Nitrous acid	HNO ₂	H - 0 - N = 0	$\frac{\text{HNO}_2(aq) + \text{H}_2\text{O}(l)}{\text{H}_3\text{O}^+(aq) + \text{NO}_2^-(aq)}$	4.6×10^{-4}
Hydrofluoric acid	HF	H F	$\begin{array}{rrr} HF(aq) &+ H_2O(l) \\ & \\ H_3O^+(aq) &+ F^-(aq) \end{array}$	$3.5 imes10^{-4}$
Formic acid	HCH0 ₂	н—о—с_−н	$\begin{array}{r} \text{HCHO}_2(aq) &+ \text{H}_2\text{O}(l) \\ \\ \text{H}_3\text{O}^+(aq) &+ \text{CHO}_2^-(aq) \end{array}$	$1.8 imes 10^{-4}$
Benzoic acid	HC7H502	H-0-C-CCCCH	$\begin{array}{rl} HC_{7}H_{5}O_{2}(aq) & + H_{2}O(l) \\ H_{3}O^{+}(aq) & + C_{7}H_{5}O_{2}^{-}(aq) \end{array}$	$6.5 imes 10^{-5}$
Acetic acid	HC ₂ H ₃ O ₂	$\mathbf{H} - \mathbf{O} - \mathbf{C} - \mathbf{C} \mathbf{H}_3$	$\begin{array}{rrr} HC_{2}H_{3}O_{2}(aq) & + H_{2}O(l) \\ H_{3}O^{+}(aq) & + C_{2}H_{3}O_{2}^{-}(aq) \end{array}$	1.8×10^{-5}
Hypochlorous acid	HCIO	H-0-CI	$\begin{array}{rrr} HCIO(aq) &+ H_2O(l) & & \\ H_3O^+(aq) &+ CIO^-(aq) \end{array}$	$2.9 imes10^{-8}$
Hydrocyanic acid	HCN	$H - C \equiv N$	$\frac{\text{HCN}(aq) + \text{H}_2\text{O}(l)}{\text{H}_3\text{O}^+(aq) + \text{CN}^-(aq)}$	4.9×10^{-10}
Phenol	HC ₆ H ₅ O		$\begin{array}{rrr} HC_{6}H_{5}O(aq) & + H_{2}O(l) \\ H_{3}O^{+}(aq) & + C_{6}H_{5}O^{-}(aq) \end{array}$	$1.3 imes 10^{-10}$

Examples:

For each reaction below, determine the conjugate acid-base pairs and their relative strengths:

 $1. \hspace{0.1in} HNO_2 \hspace{0.1in} + \hspace{0.1in} CH_3CO_2^{-} \hspace{0.1in} \Longrightarrow \hspace{0.1in} CH_3CO_2H \hspace{0.1in} + \hspace{0.1in} NO_2^{-}$

2. HCN + $CHO_2^- \implies HCHO_2 + CN^-$

3. The hydrogen oxalate ion $(HC_2O_4^-)$ is amphoteric. Write a balanced equation showing how it reacts as an acid towards water and another equation showing how it reacts as a base towards water.

4. For each acid shown below, write the formula of its conjugate base:

HPO₄²⁻ _____ CH₃NH₃⁺ _____ NH₃ _____

5. For each base shown, write the formula of its conjugate acid:

HAsO4²⁻ _____ IO⁻ _____ O²⁻_____

AUTOIONIZATION OF WATER

• As discussed earlier, water can act both as an acid or base. It acts as an acid when it reacts with HCl, and it acts as a base when it reacts with NH₃:



• Therefore, water is *amphoteric*: it can act either as an acid or base. Even when pure, water can act as an acid and a base with itself, a process called *autoionization*:



• The autoionization reaction and its equilibrium constant can be written as:

 $2 \text{ H}_2 \text{O} (\text{l}) \implies \text{H}_3 \text{O}^+ (\text{aq}) + \text{OH}^- (\text{aq})$

$$\mathbf{K}_{w} = [\mathbf{H}_{3}\mathbf{O}^{+}][\mathbf{O}\mathbf{H}^{-}]$$

- This equilibrium constant is called *ion product constant for water* (K_w), and has a value of 1.0×10^{-14} at 25°C.
- In pure water, $[H_3O^+] = [OH^-]$. Therefore

 $[H_3O^+] = [OH^-] = \sqrt{K_w} = \sqrt{1.0 \times 10^{-14}}$ $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} M$

ACIDIC & BASIC SOLUTIONS

• An *acidic solution* contains an acid that creates additional H₃O⁺ ions, causing [H₃O⁺] to increase. Since the K_w value remains constant in any solution, the [OH⁻] in these solutions can be calculated as shown:

$$[H_3O^+] [OH^-] = 1.0 \times 10^{-14}$$
 $[OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]} M$

• For example, if $[H_3O^+] = 1.0 \times 10^{-3}$, then the $[OH^-]$ can be calculated as:

$$[OH] = \frac{1.0 \text{ x } 10^{-14}}{[H_3O^+]} = \frac{1.0 \text{ x} 10^{-14}}{1.0 \text{ x} 10^{-3}} \ 1.0 \text{ x} 10^{-11} \text{ M}$$

In acidic solutions $[H_3O^+] > [OH^-]$

• A *basic solution* contains a base that creates additional OH⁻ ions, causing [OH⁻] to increase. Since the K_w value remains constant in any solution, the [H₃O⁺] in these solutions can be calculated as shown:

$$[H_3O^+] [OH^-] = 1.0 \ge 10^{-14}$$
 $[H_3O^+] = \frac{1.0 \ge 10^{-14}}{[OH^-]}$

• For example, if $[OH^-] = 1.0 \times 10^{-2}$, then the $[H_3O^+]$ can be calculated as:

$$[\mathbf{H}_{3}\mathbf{O}^{+}] = \frac{1.0 \text{ x } 10^{-14}}{[\mathbf{OH}^{-}]} = \frac{1.0 \text{ x} 10^{-14}}{1.0 \text{ x} 10^{-2}} \ 1.0 \text{ x} 10^{-12} \text{ M}$$

In basic solutions
$$[OH^-] > [H_3O^+]$$

SUMMARY

> In a neutral solution: $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} M$

▷ In an acidic solution: $[H_3O^+] > [OH^-]$

$$\begin{split} [H_3O^+] > 1.0 \ x \ 10^{-7} \ M \\ [OH^-] \ < 1.0 \ x \ 10^{-7} \ M \end{split}$$

▷ In a basic solution: $[H_3O^+] < [OH^-]$

$$\begin{split} [H_3O^+] < 1.0 \ x \ 10^{-7} \ M \\ [OH^-] \ > 1.0 \ x \ 10^{-7} \ M \end{split}$$



Examples:

1. What is the concentration of the $[H_3O^+]$ and $[OH^-]$ in a 0.25 M solution of Ba $(OH)_2$?

 $\begin{array}{rcl} Ba(OH)_2\,(aq) & \longrightarrow & Ba^{2^+}(aq) & + & 2OH^-(aq) \\ 0.25 \text{ M} & & 0.25 \text{ M} & & 2 \times 0.25 \text{ M} \end{array}$ $[OH^-] = 0.50 \text{ M} \\ [H_3O^+] & = \end{array}$

2. What is the concentration of the $[H_3O^+]$ and $[OH^-]$ in a 0.040 M solution of HNO₃?

3. Identify each of the following solutions are acidic, basic or neutral:

 $[OH^{-}] = 1.0 \text{ x}10^{-5} \text{ M}$ $[H_3O^{+}] = 3.8 \text{ x}10^{-9} \text{ M}$ $[H_3O^{+}] = 6.2 \text{ x}10^{-3} \text{ M}$ $[OH^{-}] = 4.5 \text{ x}10^{-10} \text{ M}$

pH SCALE

• The pH scale is a compact way to specify the acidity of a solution. pH is defined as the negative log of hydronium ion concentration:

$\mathbf{pH} = -\log\left[\mathbf{H}_{3}\mathbf{O}^{+}\right]$

• Therefore, a solution with $[H_3O^+] = 1.0 \times 10^{-3} \text{ M}$ (acidic) has pH of:

$$pH = -\log [H_3O^+] = -\log (1.0x10^{-3}) = -(-3.00) = 3.00$$

• Note that the significant digits in a logarithm appear after the decimal. Therefore, the 2 significant figures in the [H₃O⁺] appear as 2 decimal places in the pH:

	2 significant digits	2 decimal places
In general,	$\log 1.0 \times 10$	$^{-3} = 3.00$
 For a <i>neutral</i> solution For an <i>acidic</i> solution For a <i>basic</i> solution: 	n: $[H_3O^+] = 1.0 \text{ x } 1$ n: $[H_3O^+] > 1.0 \text{ x } 1$ $[H_3O^+] < 1.0 \text{ x } 1$	0^{-7} M $pH = 7.00$ 0^{-7} M $pH < 7.00$ 0^{-7} M $pH > 7$

- Listed on the right is the pH of some common substances. As discussed earlier, many foods are acidic and have low pH values. Few foods are basic.
- Note that:
 - since pH is a negative scale, a lower pH value indicates greater H₃O⁺ concentration,

and

• since pH is a logarithmic scale, a change of 1 pH corresponds to a 10-fold change in H_3O^+ concentration.

Substance	рH
Gastric juice (human stomach)	1.0-3.0
Limes	1.8-2.0
Lemons	2.2-2.4
Soft drinks	2.0-4.0
Plums	2.8-3.0
Wines	2.8-3.8
Apples	2.9-3.3
Peaches	3.4-3.6
Cherries	3.2-4.0
Beers	4.0-5.0
Rainwater (unpolluted)	5.6
Human blood	7.3-7.4
Egg whites	7.6-8.0
Milk of magnesia	10.5
Household ammonia	10.5-11.5
4% NaOH solution	14

pH SCALE

• The relationship of pH scale and the $[H_3O^+]$ are summarized below:



Examples:

1. Obtain the pH corresponding to a hydroxide-ion concentration of 2.7×10^{-10} M.

 $[H_{3}O^{+}] =$ pH =

2. A wine was tested for acidity, and it pH was found to be 3.85 at 25 °C. What is the hydronium ion concentration?

 $\log [H_3O^+] =$ $[H_3O^+] =$

3. A 1.00 L aqueous solution contains 6.78 g of Ba(OH)₂. What is the pH of the solution?

4. What mass of HI is present in a solution with a volume of 0.250 L and pH of 1.25?

pOH & OTHER p SCALES

• The pOH scale is analogous to the pH scale but is defined with respect to the [OH⁻].

pOH = – log [OH⁻]

- Therefore, a solution with $[OH^-] = 1.0 \times 10^{-3} \text{ M}$ (basic) has pOH of 3.00.
- On the pOH scale, a pOH of less than 7 is basic, and a pOH of greater than 7 is acidic. The pH and pOH scale relationships are shown below:



• A relationship between pH and pOH can be derived from the K_w expression:

$$[H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Taking the log of both sides:

$$\log [H_3O^+] + \log [OH^-] = -14.00$$
$$- \log [H_3O^+] - \log [OH^-] = 14.00$$
$$pH + pOH = 14.00$$

• Another common p scale is the pK_a scale, defined as:

<mark>pK_a = – log K</mark>a

• The pK_a of an acid is another way to quantify its strength. The smaller the pK_a , the stronger the acid. For example:

HClO ₂	$K_a = 1.1 \times 10^{-2}$	$pK_a = 1.96$
HCHO ₂	$K_a = 1.8 \times 10^{-4}$	$pK_a = 3.74$

Examples:

1. Rank the following 0.1 M solutions of acids in order of increasing ionization (lowest to highest):

H_2S	$K_a = 1.0 \text{ x } 10^{-7}$
HCN	$K_a = 6.2 \times 10^{-10}$
HNO ₂	$K_a = 7.2 \times 10^{-4}$
HOCl	$K_a = 2.9 \times 10^{-8}$

2. Rank the following 0.1 M solutions of acids in order of decreasing $[H_3O^+]$ (highest to lowest):

HF	$pK_a = 3.46$
HClO ₂	$pK_a = 1.96$
HC ₆ H ₅ O	$pK_a = 9.89$
$HC_2H_3O_2$	$pK_a = 4.74$

3. Rank

CALCULATING pH of STRONG & WEAK ACIDS

• A solution containing a strong or weak acid has two potential sources of H_3O^+ : the ionization of the acid itself and the autoionization of water:

 $\begin{array}{rll} \text{HA}(\text{aq}) \ + \ H_2 O(l) & \Longrightarrow & H_3 O^+ \ (\text{aq}) \ + \ A^- \ (\text{aq}) & & \text{Strong or Weak acid} \\ \\ 2 \ H_2 O(l) & \longmapsto & H_3 O^+ \ (\text{aq}) \ + \ OH^- \ (\text{aq}) & & K_w = 1.0 \times 10^{-14} \end{array}$

- Except in extremely dilute solutions, the autoionization of water contributes a negligibly small amount of H_3O^+ compared to the ionization of the strong or weak acid.
- Furthermore, in a strong or weak acid solution, the ionization of the acid further decreases the autoionization of water due to the shift to the right in equilibrium (as described by Le Chaterlier's principle).
- Consequently, in most strong or weak acid solutions, the H₃O⁺ produced by the autoionization of the water can be ignored.

Strong Acids:

• Since strong acids ionize completely in solution and since we can ignore the hydronium ion contribution due to autoionization of water:

 $[H_3O^+] = [HA]$ For strong acids

• For example, for a 0.10 M HCl solution:

 $[H_3O^+] = 0.10 \text{ M}$ and $pH = -\log(0.10) = 1.00$

Weak Acids:

• Finding the pH of a weak acid is more complicated, since the concentration of H_3O^+ ion is not equal to the concentration of the weak acid (due to partial ionization of the acid):

 $[H_3O^+] \neq [HA]$ For weak acids

• For example, for a 0.10 M HC₂H₃O₂ solution:

 $[{\rm H_3O^+}] < 0.10 \; M \qquad \ \ and \qquad pH = 2.87$

• Therefore, a 0.10 M solution of acetic acid is less acidic (higher pH) than 0.10 M solution of HCl.

CALCULATING pH WEAK ACIDS

- To calculate the pH of a weak acid solution requires solving an equilibrium problem similar to those in Chapter 14.
- For example, consider a generic weak acid HA with an acid ionization constant K_a . Since the $[H_3O^+]$ due to autoionization of water can be ignored, only the $[H_3O^+]$ due to the ionization of the acid must be determined:

$$HA(aq) + H_2O(l) \implies H_3O^+(aq) + A^-(aq)$$

• The initial and equilibrium concentration of all species in the above equilibrium can be summarized in an ICE table:

	[HA]	[H ₃ 0 ⁺]	[A ⁻]
Initial	0.10	pprox 0.00	0.00
Change	-x	+x	+x
Equilibrium	0.10 — x	X	X

• The equilibrium concentration of H_3O^+ can be found using the K_a as shown below:

$$K_{a} = \frac{[H_{3}O^{+}][A^{-}]}{[HA]} = \frac{x^{2}}{0.10 - x}$$

• To solve for x requires quadratic equation and formula. However, in most cases we can significantly simplify the calculation by using an approximation shown below:

Therefore:

 $0.10 - x \approx 0.10$

- It follows: $K_a = \frac{x^2}{0.10 x} = \frac{x^2}{0.10}$
- This method is commonly referred to as the "Approximation Method", and is discussed in the next examples.

CALCULATIONS WITH K_a

Examples:

1. Lactic acid, $HC_3H_5O_3$, is a weak acid found in sour milk. A 0.025 M solution of lactic acid has a pH of 2.75. What is the ionization constant, K_a for this acid? What is the degree of ionization?

	$HC_3H_5O_3(l) + H_2O(l) \iff H_3O^+(aq) + C_3H_5O_3^-(aq)$				
Initial	0.025 M		0	0	
Δ	—x		+x	+x	
Equilibrium	0.025–x		х	х	

$$\mathbf{K}_{a} = \frac{[\mathbf{H}_{3}\mathbf{O}^{+}][\mathbf{C}_{2}\mathbf{H}_{3}\mathbf{O}_{2}^{-}]}{[\mathbf{H}\mathbf{C}_{2}\mathbf{H}_{3}\mathbf{O}_{2}]} = \frac{\mathbf{x}^{2}}{0.025 - \mathbf{x}}$$

$$[H_3O^+] = x = antilog (-pH) = antilog (-2.75) = 1.78 \times 10^{-3}$$

 $[C_3H_5O_3^{-}] = x = 1.\underline{78} \times 10^{-3}$

$$[HC_{3}H_{5}O_{3}] = (25 \text{ x } 10^{-3}) - (1.\underline{7}8 \text{ x } 10^{-3}) = 23.2 \text{ x } 10^{-3}$$

$$K_{a} = \frac{(1.78 \text{ x } 10^{-3})^{2}}{23.2 \text{ x } 10^{-3}} = 1.4 \text{ x } 10^{-4}$$

Molar concentration of Ionized Acid

Degree of Ionization =

Total Molar concentration of Acid

Degree of Ionization = $\frac{1.78 \times 10^{-3}}{25 \times 10^{-3}} = 0.071$ or 7.1%

Examples:

2. What are the concentrations of hydrogen ion and acetate ion in a solution of 0.10 M acetic acid? What is the pH of the solution? What is the degree of ionization? (K_a of acetic acid = 1.7 x 10⁻⁵)

	$HC_2H_3O_2(l) + H_2O(l) \iff H_3O^+(aq) + C_2H_3O_2^-(aq)$				
Initial	0.10		0	0	
Δ	—x		+x	+x	
Equilibrium	0.10–x		х	х	

$$K_{a} = \frac{[H_{3}O^{+}][C_{2}H_{3}O_{2}^{-}]}{[HC_{2}H_{3}O_{2}]} = \frac{x^{2}}{0.10-x} = 1.7 \times 10^{-5}$$

Using the approximation method:

 $K_a = \frac{x^2}{0.10} = 1.7 \text{ x } 10^{-5} \text{ It follows:}$ $x^2 = 1.7 \text{ x } 10^{-6}$

 $x = [H_3O^+] = [C_2H_3O_2^-] = 1.30 \times 10^{-3} M$

pH = - log (H₃O⁺) = - log (1.30 x 10⁻³) = 2.89
Degree of Ionization =
$$\frac{1.30 \times 10^{-3}}{1.0 \times 10^{-1}}$$
 = 0.013 or 1.3%

• The approximation assumption can be checked for validity:

 $0.10 - x \approx 0.10$ is valid or not

0.10 - 0.00130 = 0.09870 = 0.10 YES, the assumption is valid!

Examples: 3. Calculate the pH and % ionization of a 0.250 M solution of HF. ($K_a = 3.5 \times 10^{-4}$)

Initial		
Δ		
Equilibrium		

MIXTURE OF ACIDS

• Finding the pH of a mixture of acids depends on the relative strength and degree of ionization of each acid. Three types of mixtures will be studied in this section.

Mixture of Two Strong Acids

• Since both acids ionize completely, the hydronium ion concentration of each must be considered in this case.

Examples:

1. Determine the pH of a solution prepared by mixing 150 mL of a 0.12M solution of HCl with 250 mL of a 0.18M solution of HNO₃.

2. Determine the pH of a solution prepared by adding 120 mL of a solution of HBr with pH of 3.75 with 180 mL of a solution of HCl with pH of 4.30.

MIXTURE OF ACIDS

Mixture of Two Weak Acids

- When two weak acids are mixed, since each ionizes partially, the ionization of each must be considered when determining the hydronium ion concentration. However, the situation can be greatly simplified if the difference in the K_a of the two acids is 10^2 or greater.
- In these instances, the pH is determined based on the $[H_3O^+]$ of the stronger acid using ionization equilibrium method studied earlier.
- The [H₃O⁺] produced by the stronger acid suppresses the ionization of the weaker acid, and must be considered in determining the concentration of the anion produced by the weaker acid.

Examples10

1. Determine the pH and the [CN⁻] of a solution that contains 1.00 M HCN ($K_a = 6.2 \times 10^{-10}$) and 5.00 M HNO₂ ($K_a = 4.0 \times 10^{-4}$).

2. Determine the pH and the $[OC_6H_5^-]$ of a solution that contains 1.0 M HF (K_a= 7.2x10⁻⁴) and 1.0 M HOC₆H₅ (K_a= 1.6x10⁻¹⁰).

POLYPROTIC ACIDS

• Polyprotic acids are acids that can release more than one H⁺ per molecules of acid

Examples:

1. <u>H₂SO₄ (strong acid) and HSO₄ (weak acid)</u>

H ₂ SO ₄ (aq)	+	H ₂ O (l)	$\xrightarrow{\text{complete dissociation}} \rightarrow$	$H_3O^+(aq)$	+	HSO ₄ ⁻ (aq)
HSO ₄ ⁻ (aq)	+	H ₂ O (l)	$\xrightarrow{\text{partial dissociation}}$	$H_3O^+(aq)$	+	SO ₄ ²⁻ (aq)

2. H_2CO_3 (weak acid) and HCO_3^- (weak acid)

$$H_2CO_3(aq) + H_2O(l)$$
 \leftarrow $H_3O^+(aq) + HCO_3^-(aq)$ $K_a = 4.3 \times 10^{-7}$

$$HCO_3^{-}(aq) + H_2O(l) \qquad \longleftarrow \qquad H_3O^{+}(aq) + CO_3^{2-}(aq) \qquad \qquad K_a = 4.8 \times 10^{-11}$$

$$H_3PO_4(aq) + H_2O(l) \longleftarrow H_3O^+(aq) + H_2PO_4^-(aq) K_a = 6.9 \times 10^{-3}$$

$$H_2PO_4^-(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + HPO_4^{2-}(aq) \qquad K_a = 6.2 \times 10^{-8}$$

$$HPO_4^{2-}(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + PO_4^{3-}(aq) K_a = 4.8 \times 10^{-13}$$

 $\underline{\text{NOTE:}} \qquad \qquad \mathbf{K_{a1} > K_{a2} > K_{a3}}$

Meaning:	A diprotic acid	- loses the first H ⁺ easier than the second one.
	A triprotic acid:	- loses the first H ⁺ easier than the second one
		- loses the second H ⁺ easier than the third one.

Reason: The $1^{st} H^+$ separates from an ion of a single negative charge The $2^{nd} H^+$ separates from an ion of an ion of a double negative charge The $3^{rd} H^+$ separates from an ion of a triple negative charge

CALCULATING THE CONCENTRATION OF VARIOUS SPECIES IN A SOLUTION OF A POLYPROTIC ACID

Ascorbic acid (H₂Asc) is a diprotic acid with $K_{a1} = 7.9 \times 10^{-5}$ and $K_{a2} = 1.6 \times 10^{-12}$. What is the pH of a 0.10 M solution of ascorbic acid? What is the concentration of the ascorbate ion (Asc^{2-}) , in the solution?

First Part: Calculate the pH of the solution:

- Note that K_{a2} (1.6 x 10⁻¹²) <<<<<< K_{a1} (7.9 x 10⁻⁵)
- As such:
- the 2^{nd} ionization can be neglected any H⁺ produced by the 2^{nd} ionization can be ignored.

	H_2Asc (aq)	+ H_2O (l) \Leftarrow	\Rightarrow H ₃ O ⁺ (aq) +	HAsc ⁻ (aq)
Initial	0.10 M		0	0
Δ	—x		+x	+x
Equilibrium	0.10–x		x	x

$$K_{a1} = \frac{[H_3O^+][HAsc^-]}{[H_2Asc]} = \frac{x^2}{0.10-x} = 7.9x10^{-5}$$
$$x^2 = (0.10)(7.9x10^{-5}) = 7.9x10^{-6} \qquad x = [H_3O^+] = 2.8x10^{-3}$$
$$pH = -\log(2.8x10^{-3}) = 2.55$$

Second Part: Calculate the concentration of the sulfite ion (SO_3^{2-}) :

$H_2Asc(aq) +$	$H_2O(l)$	→	HAsc ⁻ (aq) + $H_3O^+(aq)$	$K_{a1} = 7.9 \text{ x} 10^{-5}$

HAsc⁻(aq) + H₂O(1) \checkmark Asc²⁻(aq) + H₃O⁺(aq) $K_{a2} = 1.6 \times 10^{-12}$

	HAsc ⁻ (aq) -	+ H_2O (l) \Leftarrow	\Rightarrow H ₃ O ⁺ (aq)	+ $Asc^{2-}(aq)$
Initial	0.0028		0.0028	0
Δ	—у		+y	+y
Equilibrium	0.0028 - y		0.0028 + y	у

$$K_{a2} = \frac{[H_3O^+][Asc^{2-}]}{[HAsc^-]} = \frac{(0.0028 + y)(y)}{0.0028 - y} = 1.6x10^{-12}$$



$$K_{a2} = \frac{(0.0028 + y)(y)}{0.0028 - y} = \frac{(0.0028)(y)}{0.0028} = 1.6x10^{-12}$$

 $y = [Asc^{2-}] = 1.6 \times 10^{-12} M$

• General Rule: The concentration of the ion A^{2–} equals the second ionization constant, Ka₂

Examples:

1. Carbonic acid (H₂CO₃) is a weak acid with $K_{a1} = 4.3 \times 10^{-7}$ and $K_{a2} = 4.8 \times 10^{-11}$. Calculate the pH and the carbonate ion concentration of a 0.050M solution of carbonic acid.

STRONG BASES

• Similar to a strong acid, a *strong base* is defined as one that ionizes completely. For example, NaOH is a strong base:

NaOH (aq) \longrightarrow Na⁺ (aq) + OH⁻ (aq)

- As a result, a 1.0 M NaOH solution has $[OH^-] = [Na^+] = 1.0$ M.
- Listed below are some common strong bases. Most strong bases are group 1 and 2 metal hydroxides.

TABLE 15.7 Strong Bases	
Lithium hydroxide (LiOH)	Strontium hydroxide [Sr(OH) ₂]
Sodium hydroxide (NaOH)	Calcium hydroxide [Ca(OH) ₂]
Potassium hydroxide (KOH)	Barium hydroxide [Ba(OH) ₂]

• When group 2 hydroxides dissolve in water, they produce 2 mol of OH⁻per mole of base. For example:

 $Sr(OH)_2 \ (aq) \ \longrightarrow \ Sr^{2+} \ (aq) \ + \ 2 \ OH^- \ (aq)$

• Unlike diprotic acids, which ionize in two steps, these bases ionize in one step.

Examples:

- 1. Determine the $[OH^-]$, $[H_3O^+]$, pH and pOH for each strong base shown below:
 - a) 0.0015 M Sr(OH)₂
 - b) 3.85% by mass KOH (d= 1.01 g/mL)



WEAK BASES

• Similar to weak acids, *weak bases* ionize partially in water. Unlike strong bases that contain OH⁻, the most common weak bases produce OH⁻ by accepting a proton from water, as shown below:

 $B(aq) + H_2O(l) \implies BH^+(aq) + OH^-(aq)$

$$NH_3(aq) + H_2O(l) \implies NH_4^+(aq) + OH^-(aq)$$

- Since the ionization of a weak base is incomplete, it follows that a 1.0 M NH₃ solution will have $[OH^-] < 1.0$ M.
- The extent of the ionization of a weak base is quantified with the base ionization constant (K_b). For the general reaction in which a weak base ionizes, K_b is defined as:

$$\mathbf{K}_{\mathbf{b}} = \frac{[\mathbf{B}\mathbf{H}^+][\mathbf{O}\mathbf{H}^-]}{[\mathbf{B}]}$$

• Listed below are some common weak bases, and their corresponding K_b values. Similar to weak acids, the "p" scale can also be applied to bases, with $pK_b = -\log K_b$. Note that most weak bases are ammonia or amine derivatives. These are nitrogen containing compounds with a lone pair of electrons on N, which serves as a proton acceptor:

$$H = \begin{array}{c} H & H & H \\ I & H \\ C & -\ddot{N} - H(aq) + H - \ddot{O} - H(l) \end{array} \longrightarrow \begin{array}{c} H & H & H \\ I & I \\ H & H \end{array} H = \begin{array}{c} H & -\dot{O} - N^{+} - H(aq) + : \ddot{O} - H(l) \\ I & I \\ H & H \end{array}$$

Weak Base	Ionization Reaction	K _b (at 25 °C)
Carbonate ion $({\rm CO_3}^{2-})^*$	$\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \iff \text{HCO}_3^{-}(aq) + \text{OH}^{-}(aq)$	1.8×10^{-4}
Methylamine (CH_3NH_2)	$CH_3NH_2(aq) + H_2O(l) \iff CH_3NH_3^+(aq) + OH^-(aq)$	4.4×10^{-4}
Ethylamine (C ₂ H ₅ NH ₂)	$C_2H_5NH_2(aq) + H_2O(I) \Longrightarrow C_2H_5NH_3^+(aq) + OH^-(aq)$	$5.6 imes 10^{-4}$
Ammonia (NH ₃)	$NH_3(aq) + H_2O(I) \Longrightarrow NH_4^+(aq) + OH^-(aq)$	$1.76 imes 10^{-5}$
Bicarbonate ion (HCO ₃ ⁻) [*] (or hydrogen carbonate)	$HCO_{3}^{-}(aq) + H_{2}O(l) \iff H_{2}CO_{3}(aq) + OH^{-}(aq)$	2.3×10^{-8}
Pyridine (C ₅ H ₅ N)	$C_5H_5N(aq) + H_2O(I) \Longrightarrow C_5H_5NH^+(aq) + OH^-(aq)$	1.7×10^{-9}
Aniline (C ₆ H ₅ NH ₂)	$C_{e}H_{e}NH_{2}(aa) + H_{2}O(I) \iff C_{e}H_{e}NH_{2}^{+}(aa) + OH^{-}(aa)$	$3.9 imes 10^{-10}$



CALCULATIONS WITH K_b

• Finding the [OH⁻] and pH of a weak base is similar to that of a weak acid. As with the weak acids, the contribution of the [OH⁻] by autoionization of water can be ignored, and only the [OH⁻] produced by the bases will be considered.

Examples:

1. What is the pH of a 0.20 M solution of ammonia in water ($K_b = 1.8 \times 10^{-5}$)?

	NH ₃ (aq)	+ H_2O (l) \Leftarrow	\Rightarrow NH ₄ ⁺ (aq) +	OH ⁻ (aq)
Initial	0.20 M		0	0
Δ	—x		+x	+x
Equilibrium	0.20–x		x	х

Assume that x is small enough to neglect compared with 0.20.

$$K_{b} = \frac{[NH_{4}^{+}][OH^{-}]}{[NH_{3}]} = \frac{x^{2}}{0.20-x} = \frac{x^{2}}{0.20} = 1.8 \times 10^{-5}$$
 $x^{2} = 3.6 \times 10^{-6}$

 $x = [OH^{-}] = 1.89 \times 10^{-3} M$ (Note that x is negligible compared to 0.20)

$$[H_{3}O^{+}] = \frac{1.0 \times 10^{-14}}{1.89 \times 10^{-3}} = 5.3 \times 10^{-12} \qquad pH = -\log(5.3 \times 10^{-12}) = 11.28$$

2. Quinine is an alkaloid, or naturally occurring base, used to treat malaria. A 0.0015 M solution of quinine has a pH of 9.84. What is K_b of quinine?

pOH = 14.00 - pH = 14.00 - 9.84 = 4.16[OH⁻] = antilog (-4.16) = 6.92 x 10⁻⁵ M

	Qu (aq) +	H_2O (l) \leftarrow	$ \ge HQu^+(aq) + $	OH ⁻ (aq)
Initial	0.0015 M		0	0
Δ	—x		+x	+x
Equilibrium	0.0015-x		Х	Х

$$K_{b} = \frac{[HQu^{+}][OH^{-}]}{[Qu]} = \frac{x^{2}}{0.0015 - x} = \frac{(6.92 \times 10^{-5})^{2}}{(0.0015 - 6.92 \times 10^{-5})} = 3.3 \times 10^{-6}$$

RELATIONSHIP BETWEEN K_a AND K_b

• The quantitative relationship between an acid and its conjugate base can be seen in the examples below:

 $NH_4^+(aq) + H_2O(l) \iff H_3O^+(aq) + NH_3(aq)$

 $NH_3(aq) + H_2O(l) \implies NH_4^+(aq) + OH^-(aq)$

• Each of these equilibria can be expressed by an ionization constant:

$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]}$$
 and $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$

• Addition of the two equations above results the following:

$$\frac{\mathrm{NH}_{4}^{+}(\mathrm{aq}) + \mathrm{H}_{2}\mathrm{O}(\mathrm{l})}{\mathrm{NH}_{3}(\mathrm{aq}) + \mathrm{H}_{2}\mathrm{O}(\mathrm{l})} \stackrel{\longrightarrow}{\longrightarrow} \mathrm{H}_{3}\mathrm{O}^{+}(\mathrm{aq}) + \mathrm{OH}^{-}(\mathrm{aq})}{\mathrm{K}_{b}}$$

$$\frac{\mathrm{NH}_{3}(\mathrm{aq}) + \mathrm{H}_{2}\mathrm{O}(\mathrm{l})}{\mathrm{2}\mathrm{H}_{2}\mathrm{O}(\mathrm{l})} \stackrel{\longrightarrow}{\longrightarrow} \mathrm{H}_{3}\mathrm{O}^{+}(\mathrm{aq}) + \mathrm{OH}^{-}(\mathrm{aq})}{\mathrm{K}_{w}}$$

• Recall that when two reactions are added to form a third reaction, the equilibrium constant for the third reaction is the products of the two added reactions. Therefore,

$$\mathbf{K}_{\mathbf{w}} = \mathbf{K}_{\mathbf{a}} \mathbf{x} \mathbf{K}_{\mathbf{b}}$$

• Note that K_a and K_b are inversely proportional for an acid-base conjugate pair. This is expected, since as the strength of an acid increases (larger K_a), the strength of its conjugate base decreases (smaller K_b).

Examples:

1. Hydrofluoric acid (HF) has $K_a = 6.8 \times 10^{-4}$. What is K_b for the fluoride ion?

$$K_b = \frac{K_w}{K_a} =$$

2. Which of the following anions has the largest K_b value: NO₃⁻, PO₄³⁻, HCO₃⁻?

ANIONS AS WEAK BASES

• Any anion can be thought of as the conjugate base of an acid. Consider the following anions and their corresponding acids:

<u>anion</u>	<u>conjugate acid</u>
Cl	HCl
F^-	HF
NO_3^-	HNO ₃
$C_2H_3O_2^-$	$HC_2H_3O_2$

- Since any anion can be regarded as the conjugate base of an acid, every anion can *potentially* act as a base. Whether an anion acts as a base or not depends on the strength of the corresponding acid.
- In general,
 - An anion that is the conjugate base of a *weak acid* will act as a *weak base*.
 - An anion that is the conjugate base of a *strong acid* will be *pH-neutral* (forms solutions that are neither acidic nor basic).
- For example, since Cl⁻ is the conjugate base of a strong acid (HCl), it is pH-neutral. However, since F⁻ is the conjugate base of a weak acid (HF), it will act as a weak base and ionizes water as shown below:

$$F^{-}(aq) + H_2O(l) \implies HF(aq) + OH^{-}(aq)$$

• This behavior of the F⁻ anion can be explained by reviewing the ionization of its conjugate acid:

$$HF(aq) + H_2O(l) \implies H_3O^+(aq) + F^-(aq)$$

- Since HF is a weak acid, it ionizes partially. Therefore, the equilibrium above favors the left side. This can also be explained by the fact that F⁻ has a significant affinity for H⁺ ions. Therefore, when F⁻ is placed in water, it removes H⁺ ion from water, acting as a base.
- Shown on the right is a list of acids and their conjugate base anions. Note that as the strength of the acid increases, the strength of the conjugate base decreases.

			Acid	Base		
			HCl	Cl ⁻		
		Strong	H_2SO_4	HSO_4^-	Neutral	
		strong	HNO3	NO_3^-		
			H_3O^+	H ₂ O		
			HSO_4^-	SO_4^{2-}		
			H_2SO_3	HSO ₃ ⁻		
			H ₃ PO ₄	$H_2PO_4^-$		
ے		H	HF	F ⁻		
angt			HC ₂ H ₃ O ₂	$C_2H_3O_2^-$		ase
Stre			H_2CO_3	HCO ₃ ⁻	Weak	Stre
Acid		Weak	H ₂ S	HS ⁻		ngti
-			HSO ₃ ⁻	SO_3^{2-}		-
			$H_2PO_4^-$	HPO_4^{2-}		
			HCN	CN^{-}		
		$\mathrm{NH_4}^+$	NH3			
		HCO ₃ ⁻	CO_{3}^{2-}			
		HPO_4^{2-}	PO_4^{3-}			
			H ₂ O	OH-		
		Negligible	HS ⁻	S ²⁻	Strong	
		regigible	OH-	O ²⁻		

ANIONS AS WEAK BASES

• The pH of a solution of an anion acting as a base can be calculated similar to the pH determination of any weak base. The K_b for the anion acting as a base can be determined from the K_a of the conjugate acid, by the relationship discussed previously:

$$\mathbf{K}_{\mathbf{w}} = \mathbf{K}_{\mathbf{a}} \mathbf{x} \mathbf{K}_{\mathbf{b}}$$

Examples:

- 1. Classify each anion listed below as a weak base or pH-neutral:
 - a) NO_3^-
 - b) CHO_2^-
 - c) ClO_4^{-}
- 2. Calculate the pH of a 0.100 M NaCHO₂ solution. (K_a for HCHO₂ = 1.8x10⁻⁴)
 - **<u>Step 1:</u>** Write a balanced equation for the reaction of the anion with water. (Cation can be ignored)

 $CHO_2^-(aq) + H_2O(l) \implies HCHO_2(aq) + OH^-(aq)$

<u>Step 2:</u> Set up and complete an ICE table:

	[CH02 ⁻]	[HCH0 ₂]	[OH ⁻]
Initial	0.100	0.00	pprox 0.00
Change			
Equil			

<u>Step 3:</u> Calculate the K_b for the anion:

$$K_{b} = \frac{K_{w}}{K_{a}} =$$

<u>Step 4:</u> Solve for [OH[–]] and calculate pH of solution:

CATIONS AS WEAK ACIDS

- In contrast to anions, cations can in some cases act as weak acids. Cations, in general, can be divided into 3 types:
 - 1. Cations that are counterions of strong bases.
 - 2. Cations that are conjugate acids of weak bases.
 - 3. Cations that are small, highly charged metal ions.

1. Cations that are counter ions of strong bases:

- Strong bases such as NaOH or Ca(OH)₂ generally contain hydroxide ion and a counterion. Although these ions interact with water molecules by ion-dipole forces, they do not contribute to the acidity or basicity of the solution.
- In general, cations that are counterions of strong bases are pH-neutral and form neither acidic nor basic solutions.

2. <u>Cations that are conjugate acids of weak bases:</u>

• A cation can be formed from any nonionic weak base by adding a proton to its formula. For example:

<u>cation</u>	<u>weak base</u>
$\mathrm{NH_4}^+$	NH ₃
$C_2H_5NH_3^+$	$C_2H_5NH_2$
$CH_3NH_3^+$	CH ₃ NH ₂

• Any of these cations with the general formula BH⁺, will act as a weak acid as shown below:

 $BH^{+}\left(aq\right) \ + \ H_{2}O\left(l\right) \ \Longrightarrow \ H_{3}O^{+}\left(aq\right) \ + \ B\left(aq\right)$

• In general, a cation that is the conjugate acid of a weak base is a weak acid. The pH of a solution of these cations can be calculated similar to the pH calculations of a weak acid. The K_a for the cation acting as an acid can be determined from the K_b of the conjugate base, by the relationship discussed previously.

3. <u>Cations that are small, highly charged metals:</u>

• Small, highly charged metal cations such as Fe³⁺ and Al³⁺ form weakly acidic solutions. For example, when Al³⁺ is dissolved in water, it becomes hydrated as shown below:

$$\mathrm{Al}^{3+}\left(aq\right) \ + \ 6 \ \mathrm{H_2O}\left(l\right) \ \longrightarrow \ \mathrm{Al}(\mathrm{H_2O})_6^{\ 3+}\left(aq\right)$$

• The hydrated form of the ion then acts as a Brønsted-Lowry acid:

$$Al(H_2O)_6^{3^+}(aq) + H_2O(aq) \implies Al(H_2O)_5(OH)^{2^+}(aq) + H_3O^+(aq)$$

CLASSIFYING SALT SOLUTOIONS AS ACIDIC, BASIC OR NEUTRAL

- Since salts contain both a cation and an anion, they can form acidic, basic or neutral solutions when they dissolve in water. The pH of the solution depends on the specific cation or anion involved.
- There are four possibilities:
 - **1.** Salts in which neither cation nor anion acts as an acid or base form pH-neutral solutions

In these cases,

cation = counterion of a strong base anion = conjugate base of a strong acid Examples: NaCl $Ca(NO_3)_2$ KBr

2. Salts in which the cation does not act as an acid and the anion acts as a base form basic solutions.

In these cases,			
	cation = c $anion = c$	counterion of a strong b onjugate base of a weak	ase s acid
Examples:	NaF	$Ca(C_2H_3O_2)_2$	KNO ₂

CLASSIFYING SALT SOLUTOIONS AS ACIDIC, BASIC OR NEUTRAL

3. Salts in which the cation acts as an acid and the anion does not act as a base form acidic solutions.

In these cases,

cation = conjugate acid of a weak base or small, highly charged metal anion = conjugate base of a strong acid

Examples: $FeCl_3$ $Al(NO_3)_3$ NH_4Br

4. Salts in which the cation acts as an acid and the anion acts as a base form solutions. In which the pH depends on the relative strengths of the acid and the base.

In these cases,	cation = c anion = co	onjugate acid of a weal onjugate base of a weak	c base or small, hig c acid	hly charged metal
Examples:	FeF ₃	$\mathbf{Al}(\mathbf{C}_{2}\mathbf{H}_{3}\mathbf{O}_{2})_{3}$	NH ₄ NO ₂	

Summary:

TABLE 15.9 pH of Salt Solutions				
		ANI	NION	
		Conjugate base of strong acid	Conjugate base of weak acid	
	Conjugate acid of weak base	Acidic	Depends on relative strengths	
CATION	Small, highly charged metal ion	Acidic	Depends on relative strengths	
	Counterion of strong base	Neutral	Basic	

Examples:

1. For each of the following salts, indicate whether the aqueous solution will be acidic, basic or neutral.

Salt	Cation acts as:	Anion acts as:	Solution of salt is:
SrCl ₂			
AlBr ₃			
CH ₃ NH ₃ NO ₃			
NaCHO ₂			
NH ₄ F			

2. Household bleach is a 5% solution of sodium hypochlorite (NaClO). This corresponds to a molar concentration of about 0.70 M NaClO. What is the pH of household bleach? $(K_a \text{ for HClO} = 3.5 \text{ x } 10^{-8})$

	ClO ⁻ (aq) +	$H_2O(l)$ \Leftarrow	\Rightarrow HClO(aq) +	OH ⁻ (aq)
Initial	0.70		0	0
Δ	—x		+x	+x
Equilibrium	0.70–x		x	х

- The strength of an acid depends on how easily a H^+ is removed from the H Y bond.
- Ease of H⁺ loss is determined by 2 factors:

Polarity of the H–Y bond Strength of the H–Y bond

• To be acidic, the HY bond must be polar with H atom as the positive pole.

$$\delta^+H-Y\delta^-$$

• As a result, compare the following bonds and their corresponding dipole moments:



Not acidic

Not acidic

Acidic

<u>The Polarity of the H – Y bond</u>

• The polarity of the H–Y bond depends on the ΔEN (electronegativity difference) between the atoms involved in the bond



<u>The strength of the H – Y bond</u>

• The strength of the H - Y bond depends on the size of Y (smaller atoms form stronger bonds)



Trends among Binary Acids (HY)

- 1. <u>Across a period going from left to right</u>
 - The polarity of the H–Y bond determines this trend.

Electronegativity of Y increases

➢ Polarity of the H−Y increases

Consequently:

- $\succ H_2S \text{ is a weaker acid than HCl} \qquad H_2S < \text{HCl}$
- 2. <u>Going down a group</u>
 - The strength of the H–Y bond determines this trend

Acid	Bond Energy (kJ/mol)	Type of Acid
H—F	565	Weak
H-CI	431	Strong
H — Br	364	Strong

• The diagram below illustrates the combined effect of bond polarity and strength on the acids of group VI and VII.



Trends among Oxoacids

• Oxoacids are O containing acids



- The polarity of the H O bond determines the relative acidic strength
- The polarity of the H—O bond depends on 2 factors:

The Electronegativity of the Y atom



Acid	Electronegativity of Y	Ka
H-0-I	2.5	$2.3 imes10^{-11}$
H-O-Br	2.8	$2.0 imes10^{-9}$
H-0-CI	3.0	$2.9 imes10^{-8}$

• Chlorine is the most electronegative of the 3 elements and the corresponding acid has a greatest Ka.

The number of O atoms bonded to Y



• The greater the number of oxygens bonded to Y, the stronger the acid.

Acid	Structure	Ka
HCIO ₄	$\mathbf{H} - 0 - 0 = 0$	Strong
HCIO ₃	$\mathbf{H} - 0 - \mathbf{C} \mathbf{I} = 0$	1
HCIO ₂	H - 0 - CI = 0	$1.1 imes 10^{-2}$
HCIO	H CI	$2.9 imes10^{-8}$

Examples: 1. Which of the protons shown in red is more acidic?

$$\begin{array}{ccc} O & H \\ \parallel & & \parallel \\ H - C - O - H & H - C - O - H \\ & & \parallel \\ & & H \\ (a) & (b) \end{array}$$

• Some organic compounds act as weak acids since they contain acidic hydrogens. Among these are carboxylic acids and alcohols.



- As can be seen from the pK_a values given, carboxylic acids are the stronger acids than alcohols. This is due to 2 factors:
 - 1. The presence of the neighboring oxygen in the carboxyl group.



2. The *electron delocalization* of the anion due to *resonance hybridization*.



• The strength of similar acids can also be influenced by the presence of substituents on the neighboring atoms. For example, consider the carboxylic acids shown below:



- Although the acidic proton for each of the following carboxylic acids is attached to the same oxygen atom, they have different pK_a values, indicating different strengths.
- Looking more closely at the structure of the carbon next to the carbonyl group, we can note that they each have different substituent (H, Br, Cl, F). The more electronegative the substituent is, the more it withdraws electrons from the oxygen bonded to the acidic H, making it a stronger acid. This effect is called *inductive electron withdrawal*.
- The effect a substituent has on the acidity of a compound decreases as the distance between the substituent and the acidic proton inccreases. For example,



Examples:

1. Shown below are several molecules that can act as weak acids. Identify the acidic hydrogen in each molecule.



3. List the following compounds from the strongest acid to weakest acid:



4. Identify the acidic hydrogens in the compound below and rank in decreasing order of strength. Provide rationale for your choices.



SUMMARY OF FACTORS AFFECTING ACID STRENGTH

- Size: As the atom attached to the hydrogen increases in size (going down a group), the strength of the acid increases, due to the weakening of the bond.
- Electronegativity: As the atom attached to the hydrogen increases in electronegativity (going across a period), the strength of the acid increases.
- **Electronegativity:** As the atom attached to the hydrogen increases in electronegativity (going across a period), the strength of the acid increases.



Inductive electron withdrawal: An electron withdrawing group increases the strength of the acid. As the electronegativity of the electron withdrawing group increases and moves closer to the acidic hydrogen, the strength of the acid increases.



Examples:

- 1. Which member of each of the following pair is the stronger acid?
 - a) NH_3 and PH_3
 - b) HI and H_2Te
 - c) H_2SO_3 and H_2SeO_3
 - d) HBrO₄ and HBrO₃
 - e) HBr and H₂Se
- 2. List the following compounds in order of increasing acid strength:
 - a) HBr, H₂Se, H₂S
 - b) HBrO₃, HClO₂, HBrO
- 3. In each pair below, determine the stronger acid:
 - a) CH_3CHCH_2OH or CH_3CHCH_2OH **F Br**

b) Cl Cl

$$CH_3CCH_2OH$$
 or CH_2CHCH_2OH
 CH_3CCH_2OH or CH_2CHCH_2OH

4. For each pair below, determine which is the stronger base:

a)
$$\begin{array}{c} O & O \\ \parallel \\ CH_3CHCO^- \text{ or } CH_3CHCO^- \\ \parallel \\ Br & F \end{array}$$

b)
$$\begin{array}{c} O & O \\ \parallel \\ CH_3CHCH_2CO^- \text{ or } CH_3CH_2CHCO^- \\ \parallel \\ CI & CI \end{array}$$

Answers to In-Chapter Problems:

Page	Example No.	Answer
4	1	C_6H_5OH (acid); $C_2H_5O^-$ (base)
	2	H_2O (acid); Cl^- (base)
5	1a	$H_2SO_4 \text{ (acid)}; H_2O \text{ (base)} \rightarrow HSO_4^- \text{ (Conj base)}; H_3O^+ \text{ (conj acid)}$
	1b	HCO_3^- (base); H_2O (acid) \rightarrow H_2CO_3 (conj acid); OH^- (conj base)
	2	b
8	1	a) acid b) base c) acid d) base
	1	HNO ₂ (A); NO ₂ ⁻ (CB) $CH_3CO_2^-$ (B); CH_3CO_2H (CA)
	2	HCN (A); $CN^{-}(CB)$ $CHO_{2}^{-}(B)$; HCHO ₂ (CA)
13	3	Discussed in class
	4	PO_4^{3-} CH_3NH_2 NH_2^{-}
	5	$H_2AsO_4^-$ HIO OH^-
	1	$[H_3O^+] = 2.0x10^{-14}$
	2	$[H_3O^+] = 0.040 \text{ M}$ $[OH^-] = 2.5 \times 10^{-13}$
17	3	$\begin{array}{l} [OH^{-}] = 1.0 \times 10^{-5} & (basic) \\ [H_{3}O^{+}] = 3.8 \times 10^{-9} & (basic) \\ [H_{3}O^{+}] = 6.3 \times 10^{-3} & (acidic) \\ [OH^{-}] = 4.5 \times 10^{-10} & (acidic) \end{array}$
	1	$[H_3O^+] = 3.7 \times 10^{-5}$ pH= 4.43
19	2	$[H_3O^+] = 1.4 \times 10^{-4}$
	3	pH= 12.898
	4	1.8 g
21	1	$HCN < HOCl < H_2S < HNO_2$
	2	$HClO_2 > HF > HC_2H_3O_2 > HC_6H_5O$
26	3	pH= 2.03 % ionization = 3.74%
27	1	pH= 0.80
	2	pH= 4.00
28	1	$pH=1.35$ [CN ⁻]= $1.4x10^{-8}$ M
	2	pH= 1.57 $[OC_6H_5^-] = 5.9 \times 10^{-9} M$
31	1	

32	1a	$\begin{bmatrix} OH^{-} \end{bmatrix} = 0.0030 \text{ M} \text{pOH} = 2.52 \\ \begin{bmatrix} H_2 O^{+} \end{bmatrix} = 3 3 \times 10^{-12} \text{pH} = 11.48 \\ \end{bmatrix}$		
	1b	$[OH^-] = 0.693 \text{ M} \text{pOH} = 0.159 \\ [H_3O^+] = 1.44 \times 10^{-14} \text{pH} = 13.841$		
35	1	$K_b = 1.5 \times 10^{-11}$		
	2	PO ₄ ³⁻		
37	1	a) pH-neutral b) basic c) pH-neutral		
	2	pH= 8.37		
41	1	SrCl2 (neutral)AlBr3 (acidic)CH3NH3NO3 (acidic)NaCHO2 (basic)NH4F (acidic)		
	2	pH=10.65		
45	1	(a)		
48	1	Discussed in class		
	2	CH ₃ SO ₃ H (more delocalization of electrons on the anion due to resonance structures)		
	3	$\label{eq:ch3} \begin{array}{l} CH_3CHFCH_2OH > CH_3CHClCH_2OH > CH_2ClCH_2CH_2OH > \\ CH_3CH_2CH_2OH \end{array}$		
	4	Discussed in class		
50	1	a) PH_3 b) HI c) H_2SO_3 d) $HBrO_4$ e) HBr		
	2	a) $H_2S < H_2Se < HBr$ b) $HBrO < HBrO_3 < HClO_2$		
	3	a) CH ₃ CHFCH ₂ OH b) CH ₃ CCl ₂ CH ₂ OH		
	4	a) $CH_3CHBrCO_2^-$ b) $CH_3CHClCH_2CO_2^-$		